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(54) Abstract Title

Hard surface cleaning and disinfecting composition

(57) Acidic hard surface cleaning and disinfecting compositions particularly useful for the treatment of hard surfaces, particularly inclined lavatory surfaces comprise one or more nonionic surfactants, one or more quaternary ammonium surfactant compounds which have germicidal properties, one or more water-soluble or water-dispersible organic acids such as formic, lactic, glycolic, oxalic or citric acid, and water.

Preferably the nonionic surfactant is an ethoxylated alcohol. The composition may include other conventional ingredients such as a dye, perfume, pH adjuster, buffer, other surfactants and a thickener such as a polyacrylate, a saccharide, a gum or a clay.

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IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOSITIONS

The present invention relates to aqueous acidic hard surface cleaning and disinfecting compositions useful in the treatment of hard surfaces, particularly lavatory surfaces.

5 While the prior art has provided various compositions directed to cleaning and disinfecting hard surfaces, particularly lavatory surfaces there is yet a continuing need in the art for aqueous compositions which provide: satisfactory cleaning and disinfection of lavatory hard surfaces.

10 According to a first aspect of the invention there is provided an aqueous acidic hard surface cleaning and disinfecting composition which comprises:

one or more nonionic surfactants;

one or more quaternary ammonium surfactant compounds having germicidal properties;

15 one or more water soluble or water dispersible organic acids, particularly such organic acids selected from the group consisting of: formic acid, lactic acid, glycolic acid, oxalic acid and citric acid; and, water.

The aqueous acidic hard surface cleaning and disinfecting composition may optionally further include minor amounts, i.e., less than a combined total amount of 20 10%wt., of conventional additives including but not limited to: colorants such as pigments and dyes; fragrances and perfumes, pH adjusting agents, pH buffers, further deterative surfactants which are compatible with the quaternary ammonium compounds, as well as other conventional additives. Most desirably, these compositions are effective against both gram positive and gram negative bacteria.

25 The present invention also provides a method for cleaning (especially the removal of limescale deposits) and disinfecting from metal, enamel and porcelain surfaces as found on lavatory fixtures.

According to a further aspect of the invention there is provided a process for the treatment of a lavatory surface, preferably an inclined lavatory surface such as the 30 interior surface of a toilet bowl which process comprises the step of: spraying either

from a manually operated or pressurized package from 0.1 - 50 grams (preferably 1 - 20 grams) of a composition being taught herein onto the inclined lavatory surface so to permit the cleaning, sanitization and/or disinfection of the sprayed surfaces.

Preferably, this treatment is performed at least once daily for a sufficient number of treatments so to maintain the inclined lavatory surfaces in a satisfactorily clean condition.

According to another aspect of the invention there is provided a process for the treatment of a lavatory surface, preferably an inclined lavatory surface such as the interior surface of a toilet bowl, which process comprises the step of: utilizing a bottle supplied with a squirt-type dispenser to dispense from about 50 - 120 grams of a composition being taught herein onto the inclined lavatory surface so to permit the cleaning, sanitization and/or disinfection of the treated surfaces. Preferably, this treatment is performed at least once daily for a sufficient number of treatments so to maintain the inclined lavatory surfaces in a satisfactorily clean condition.

The compositions include one or more nonionic surfactants. These are well known, and any of these are expected to be useful in the inventive compositions. Exemplary useful nonionic surfactants include condensation products of alkylene oxide groups with an organic hydrophobic compound, such as an aliphatic or alkyl aromatic compound. Further exemplary useful nonionic surfactants include the polyoxyethylene ethers of alkyl aromatic hydroxy compounds, e.g., alkylated polyoxyethylene phenols, polyoxyethylene ethers of long chain aliphatic alcohols, the polyoxyethylene ethers of hydrophobic propylene oxide polymers, and the higher alkyl amine oxides

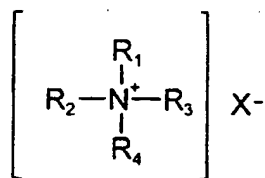
Preferred nonionic surfactants, ethoxylated alcohols are well known and may be formed by condensation of an aliphatic alcohol, or mixtures thereof, with sufficient ethylene oxide to produce a compound having a polyoxyethylene. Preferably the number of ethylene oxide units are present in an amount sufficient to insure solubility of the compound in an aqueous composition of this invention or in any dilution thereof. Desirably, the ethoxylated alcohols are produced by condensation of about 4-20, more preferably 6-18 moles of ethylene oxide with 1 mole of aliphatic alcohol. The aliphatic alcohol may be linear or may be branched, and may be a primary, secondary or tertiary alcohol (including by way of non-limiting example: decyl alcohol, dodecyl alcohol, tridecyl alcohol, hexadecyl alcohol, octadecyl alcohol, and the like). As known to those skilled in the art, the number of moles of ethylene oxide

which are condensed with one mole of aliphatic alcohol depends upon the molecular weight of the hydrophobic portion of the condensation product. The aliphatic alcohols are desirably a primary, secondary or tertiary aliphatic alcohol having about 10-20, and preferably 11-17, carbon atoms, and most preferably is an alcohol having 12 - 16 carbon atoms. Especially preferably the nonionic surfactant of the present inventive compositions is the condensation product of linear or branched C₁₂-C₁₆ aliphatic alcohols, especially C₁₂-C₁₆ linear aliphatic alcohols or mixtures thereof, with sufficient ethylene oxide to provide an average of at least 6 - 9 moles of ethylene oxide per molecule.

Also useful as nonionic surfactants are nonylphenoxy poly(ethyleneoxy) ethanols such as those materials sold under the trademark "Igepal" (ex. Rhodia). Such are particularly preferred when the inventive compositions comprise oxalic acid, or include oxalic acid as the sole organic acid.

The nonionic surfactant is present in any effective amount, but generally is present in an amount of up to about 10% by weight, based on the total weight of the composition. Desirably the nonionic surfactant is present in an amount of from about 0.01%wt. to about 5%wt, and most desirably is present in an amount of from about 0.1%wt. to about 3%wt.

The compositions according to the invention include one or more quaternary ammonium surfactant compounds having germicidal properties; these compounds provide a sanitizing effect. Particularly useful quaternary ammonium compounds and salts thereof include quaternary ammonium germicides which may be characterized by the general structural formula:

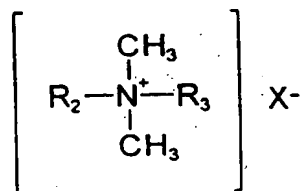


where at least one of R₁, R₂, R₃ and R₄ is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, aryl alkyl, etc. The remaining radicals on the nitrogen atoms other than the hydrophobic radicals are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon atoms.

The radicals R₁, R₂, R₃ and R₄ may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ester linkages. The radical X may be any salt-forming anionic radical.

Exemplary quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quaternary ammonium compounds which act as germicides and which are found useful in the practice of the present invention include those which have the structural formula:



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wherein R₂ and R₃ are the same or different C₈-C₁₂alkyl, or R₂ is C₁₂₋₁₆alkyl, C₈₋₁₈alkylethoxy, C₈₋₁₈alkylphenoethoxy and R₃ is benzyl, and X is a halide, for example chloride, bromide or iodide, or is a methosulfate counterion. The alkyl groups recited in R₂ and R₃ may be straight chained or branched, but are preferably substantially linear.

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Particularly useful quaternary germicides include compositions which include a single quaternary, as well as mixtures of two or more different quaternary. Particularly useful quaternary germicides include BARDAC® 205M, which is described as a mixture of alkyl dimethyl benzyl ammonium chloride/octyl decyl dimethyl ammonium chloride/didecyl dimethyl ammonium chloride/dioctyl dimethyl

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ammonium chloride; BARDAC® 208M, which is described as a mixture of alkyl dimethyl benzyl ammonium chloride and dialkyl dimethyl ammonium chloride; BTC® 885 or BTC® 888, each of which is described as a mixture of dimethyl benzyl ammonium chloride/octyl decyl dimethyl ammonium chloride/didecyl dimethyl ammonium chloride/dioctyl dimethyl ammonium chloride; BARDAC® 2050, BARDAC® 2080 or BTC® 818, each of which is described as a mixture of octyl decyl dimethyl ammonium chloride, didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride; BARDAC® 2250 and BARDAC® 2280 or BTC® 1010 which is described to be a composition which includes didecyl dimethyl ammonium chloride; BARDAC® LF and BARDAC® LF 80 which is described to be based on dioctyl dimethyl ammonium chloride; BARQUAT® MB-50, HYAMINE® 3500, BARQUAT® MB-80, BTC® 835, BTC® 8358 or BTC® 65 USP each described to be based on alkyl dimethyl benzyl ammonium chloride; BARQUAT® MX-50, BARQUAT® MX-80, BTC® 824 or BTC® 8248 each described to be a composition based on alkyl dimethyl benzyl ammonium chloride; BARQUAT® OJ-50, BARQUAT® OJ-80, BTC® 2565, or BTC® 2568 each described to be a composition based on alkyl dimethyl benzyl ammonium chloride; BARQUAT® 4250, BARQUAT® 4280, BARQUAT® 4250Z, BARQUAT® 4280Z, BTC® 2125, or BTC® 2125M each described to be a composition based on alkyl dimethyl benzyl ammonium chloride and alkyl dimethyl ethyl benzyl ammonium chloride; BARQUAT® MS-100 or BTC® 324-P-100 each described to be based on myristyl dimethyl benzyl ammonium chloride; HYAMINE® 2389 described to be based on methyl dodecyl benzyl ammonium chloride and/or methyl dodecyl xylene-bis-trimethyl ammonium chloride; HYAMINE® 1622 described to be an aqueous solution of benzethonium chloride; HYAMINE® 3500-NF or BTC® 50 each described to be based on alkyl dimethyl benzyl ammonium chloride; as well as BARQUAT® 1552 or BTC® 776 described to be based on alkyl dimethyl benzyl ammonium chloride and dialkyl methyl benzyl ammonium chloride. (Each of these recited materials are presently commercially available from Lonza, Inc., Fairlawn, NJ and/or from Stepan Co., Northfield IL).

In the cleaning compositions according to the invention, the quaternary ammonium compound constituent is required to be present in amounts which are effective in exhibiting satisfactory germicidal activity against selected bacteria sought to be treated by the cleaning compositions. Such efficacy may be achieved against

less resistant bacterial strains with only minor amounts of the quaternary ammonium compounds being present, while more resistant strains of bacteria require greater amounts of the quaternary ammonium compounds in order to destroy these more resistant strains. The quaternary ammonium compound need only be present in germicidally effective amounts, but may be present in amounts from 0.01% - 10% wt. based on the total weight of the composition of which they form a part. Desirably in the compositions of the instant invention, the quaternary ammonium compounds are present in an amount of from 0.05%wt. to about 3%wt, based on the total weight of the inventive compositions being taught herein.

An essential feature of the inventive compositions is an acid mixture comprising one or more water soluble organic acids. The acid may be present in any effective amount, but desirably is not present in amounts of more than about 10%wt. based on the total weight of the compositions. Desirably the acid mixtures form from 0.001 - 5%wt., more desirably from 0.01 - 3%wt. of the compositions, more desirably from 0.1 - 3%wt., still most desirably from about 0.5 - 2.5%wt.. The water soluble organic acids include at least one carboxyl group (-COOH) in its structure. Particularly useful as water soluble organic acids are one or more selected from formic acid, lactic acid, citric acid, oxalic acid, and glycolic acid. Sulfonic acids, such as benzenesulfonic acid, methanesulfonic acid, and para-toluenesulfonic acid are also contemplated as water soluble organic acids.

The compositions of the invention are acidic, and exhibit an acidic pH of up to about 7, more preferably a pH of about 4.5 and less and most preferably a pH in the range of from 3 - 4.5. Whereas the presence of the acid mixture described above will impart acidity to the composition, it may be desirable to include a buffer or pH adjusting agent to the compositions to maintain the compositions approximately at a desired pH (or pH range). Exemplary useful pH buffers include inorganic and organic buffering agent, and especially include alkali metal and alkaline earth metal hydroxides such as sodium hydroxide and potassium hydroxide. Others not described here may also be used. Particularly preferred is sodium hydroxide which is widely available at low cost, and is effective.

Such materials as described above are each individually known to the art, many of which are described in *McCutcheon's Emulsifiers and Detergents (Vol. 1)*, *McCutcheon's Functional Materials (Vol. 2)*, North American Edition, 1998; *Kirk-Othmer, Encyclopedia of Chemical Technology*, 3rd Ed., Vol. 22, the contents of

which are herein incorporated by reference For any particular composition described above, any optional ingredients should be compatible with the other ingredients present.

As is noted above, the compositions according to the invention are aqueous in nature. Water is added to order to provide to 100% by weight of the compositions of the invention. The water may be tap water, but is preferably distilled and is most preferably deionized water. If the water is tap water, it is preferably substantially free of any undesirable impurities such as organics or inorganics, especially minerals salts which are present in hard water which may thus undesirably interfere with the operation of the constituents present in the aqueous compositions according to the invention.

The aqueous acidic hard surface cleaning and disinfecting composition may further include minor amounts, i.e., less than a combined total amount of 10%wt., of conventional additives including but not limited to: colorants such as pigments and dyes; fragrances and perfumes, pH adjusting agents as well as other conventional additives. Most desirably, these compositions are effective against both gram positive and gram negative bacteria.

The compositions according to the invention are desirably provided as a ready to use product which may be directly applied to a hard surface. The inventive compositions are particularly useful in cleaning and disinfecting lavatory fixtures such as shower stalls, bathtubs and bathing appliances (racks, curtains, shower doors, shower bars) toilets, bidets, wall and flooring surfaces especially those which include refractory materials and the like. The inventive compositions especially particularly useful in the cleaning and disinfecting of lavatory fixtures, especially toilets and bidets. They may be packaged in any suitable container particularly flasks or bottles, including squeeze-type bottles. Desirably however, the inventive compositions are provided in a manually operable spray apparatus which is used to dispense the composition by spraying. The apparatus is also referred to as a "trigger spray" container, and may deliver the composition as a spray or "mist" of fine particles.

According to a further aspect, the present invention also provides a method for cleaning (especially the removal of limescale deposits) and disinfecting and/or sanitizing lavatory surfaces, especially vertical or inclined lavatory surfaces. Such surfaces include shower walls, shower stalls, as well as fixtures (spouts, faucets, escutcheons, plumbing handles, etc.) and especially the interior surface of a toilet

bowl. According to the process, a quantity of the compositions, e.g., from 0.1 - 50 grams, but preferably 1 - 20 grams of a composition being taught herein are sprayed via pump such as a manually operable trigger spray pump onto the inclined lavatory surface so to permit the cleaning and or sanitization of the sprayed surfaces. With the use of such a pump, the compositions are desirably sprayed from a container which delivers the composition in the form of fine droplets, such as may be supplied from a manually pumpable trigger-spray apparatus, or as which may be dispensed from a pressurized container (viz, aerosol container). Alternatively, the compositions are desirably dispensed from a different apparatus such as a conventional bottle which may include a nozzle or orifice which dispenses a liquid stream of the composition. According to this latter method, a quantity 50 - 120 grams (2 - 4 ounces) of a composition being taught herein are dispensed via the nozzle or orifice.

Preferably, this method for cleaning is performed at least once daily for a sufficient number of treatments so to maintain the inclined lavatory surfaces in a satisfactorily clean condition.

Unlike many known-art lavatory hard surface treatment compositions, the instant conditions do not include a conventional thickening constituent, specifically does not contain thickeners such as those based on polyacrylates (CARBOPOL®, available from B.F. Goodrich), naturally occurring or modified saccharides (such as cellulosed based thickeners) those based on gums (such as xanthan gum) or clays (such as laponite).

According to certain particularly preferred embodiment of the invention there is provided an aqueous acidic hard surface cleaning and disinfecting composition which comprises:

- 0.01 - 5%wt of one or more nonionic surfactants;
- one or more quaternary ammonium surfactant compounds having germicidal properties;
- one or more water soluble or water dispersible organic acids, particularly such organic acids selected from the group consisting of: formic acid, lactic acid, glycolic acid, oxalic acid and citric acid;
- optionally, to 10%wt. of one or more conventional additives such as colorants such as pigments and dyes; fragrances and perfumes, pH adjusting agents, pH buffers, further deterative surfactants which are compatible with the quaternary ammonium compounds;

and water;

wherein the compositions are essentially free of conventional thickening constituents, particularly polyacrylates, naturally occurring or modified saccharides, gums, or clays.

- 5 The aqueous acidic hard surface cleaning and disinfecting composition may further include minor amounts, i.e., less than a combined total amount of 10%wt., of conventional additives including but not limited to: colorants such as pigments and dyes; fragrances and perfumes, pH adjusting agents, pH buffers, further deterative surfactants which are compatible with the quaternary ammonium compounds, as well
10 as other conventional additives. Most desirably, these compositions are effective against both gram positive and gram negative bacteria.

The compositions according to the invention, including certain particularly preferred embodiments of the invention are presented in the following examples.

15 Examples:

- A first formulation was produced by mixing the constituents outlined in Table 1 by adding the individual constituents into a beaker of deionized water at room temperature which was stirred with a conventional magnetic stirring rod. Stirring continued until the formulation was homogenous in appearance. It is to be noted that
20 the constituents might be added in any order, but it is preferred that part of the water be the initial constituent to which the further constituents are added. The exact compositions of the example formulations are listed on Table 1, below.

Table 1	
	Ex. 1
alcohol ethoxylate	0.50
quaternary ammonium compound (80%active)	1.88
formic acid (94%active)	1.17
glycolic acid (70%active)	2.00
sodium hydroxide (50%)	2.30
fragrance	0.35
deionized water	q.s.

A second formulation was produced by mixing the constituents outlined in Table 2 by the process used to form Ex.1. The exact compositions of used to form the second formulation are listed on Table 2, below.

Table 2	Ex.2
nonylphenoxy poly(ethyleneoxy) ethanol (80% active)	1.5
quaternary ammonium compound(2) (80%active)	1.4
oxalic acid (100%)	0.5
sodium hydroxide (25%)	0.8
fragrance	0.35
deionized water	q.s.

5 The identity of the specific constituents used to produce Examples 1 and 2 are described on Table 3, following:

Table 3	
alcohol ethoxylate	GENAPOL 26-L-60 (100%wt. actives) ex. Clariant Corp.
nonylphenoxypoly(ethyleneoxy) ethanol	IGEPAL CO 730 (80%wt. active)*
quaternary ammonium compound(1) (80%active)	BTC-8358 (80% active)
quaternary ammonium compound(2) (80%active)	BARDAC 208 M (80% active)
formic acid (94%active)	aqueous dilution (94%active)
glycolic acid (70%active)	aqueous dilution (70%active)
oxalic acid (100%active)	oxalic acid (100% active)
sodium hydroxide (50%)	aqueous dilution (50%active)
sodium hydroxide (25%)	aqueous dilution (25%active)
fragrance	proprietary composition
deionized water	deionized water

The compositions are effective in the cleaning and disinfecting of hard surfaces.

Methods of Cleaning :

Example 1

10 The composition according to Ex. 1 is provided to a conventional manually operated spray dispensing container which includes a trigger spray pump. The trigger spray pump dispenses the composition in the form of a spray or "mist" of fine particles. Thereafter, 1 -50 grams of the composition is sprayed onto the surfaces of a
 15 toilet, particularly onto the inclined inner surface of the toilet bowl. This process is repeated at least once per day for a period of several days. Effective cleaning and

disinfecting of the treated surfaces as well as preventing the formation of deposits results from the process.

Example 2

5 The composition according to Ex. 2 was provided to a conventional, manually squeezable bottle provided with an orifice or nozzle which permitted the dispensing of the composition in a liquid stream. Thereafter, 56 – 120 grams (approx. 2 – 4 ounces) of the composition was sprayed onto the surfaces of a toilet, particularly onto the inclined inner surface of the toilet bowl. This process was repeated at least once per day for a period of several days. Effective cleaning and disinfecting of the treated
10 surfaces as well as preventing the formation of deposits resulted from the process.

Claims:

1. Aqueous acidic hard surface cleaning and disinfecting composition which comprises:
 - one or more nonionic surfactants;
 - one or more quaternary ammonium surfactant compounds having germicidal properties;
 - one or more water soluble or water dispersible organic acids, particularly such organic acids selected from the group consisting of: formic acid, lactic acid, glycolic acid, oxalic acid and citric acid;
 - optionally, to 10%wt. of one or more conventional additives such as colorants such as pigments and dyes; fragrances and perfumes, pH adjusting agents, pH buffers, further deterative surfactants which are compatible with the quaternary ammonium compounds;
 - water.
2. The aqueous acidic hard surface cleaning and disinfecting compositions according to claim 1 wherein the compositions are essentially free of conventional thickening constituents, particularly polyacrylates, naturally occurring or modified saccharides, gums, or clays.
3. The aqueous acidic hard surface cleaning and disinfecting composition according to claim 2 which comprises:
 - 0.01 - 5%wt of one or more nonionic surfactants;
 - one or more quaternary ammonium surfactant compounds having germicidal properties;
 - one or more water soluble or water dispersible organic acids, particularly such organic acids selected from the group consisting of: formic acid, lactic acid, glycolic acid, oxalic acid and citric acid;
 - optionally, to 10%wt. of one or more conventional additives such as colorants such as pigments and dyes; fragrances and perfumes, pH adjusting agents, pH buffers, further deterative surfactants which are compatible with the quaternary ammonium compounds;
 - and water;

wherein the compositions are essentially free of conventional thickening constituents, particularly polyacrylates, naturally occurring or modified saccharides, gums, or clays.

4. A process for the cleaning and sanitization of inclined lavatory surfaces which comprises the step of: spraying from 0.1 -50 grams of the composition according to claim 1 onto the inclined surfaces.
5. The process according to claim 4 wherein the spraying step is performed at least once daily for a sufficient number of treatments so to maintain the inclined lavatory surfaces in a satisfactorily clean condition.
6. A process for the cleaning and sanitization of inclined lavatory surfaces which comprises the step of: dispensing from 50 - 120 grams of the composition according to claim 1 onto the inclined surfaces from a container which includes an orifice or nozzle.
7. The process according to claim 6 wherein the spraying step is performed at least once daily for a sufficient number of treatments so to maintain the inclined lavatory surfaces in a satisfactorily clean condition.



Application No: GB 9908682.9
Claims searched: 1 - 7

Examiner: Michael Conlon
Date of search: 26 July 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.Q): C5D (DHX, DHZ, DJX, DFB, D120, D162, D182)
Int CI (Ed.6): C11D 3/20
Other: Online: EPODOC

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB2329901 A (Reckitt & Colman) Table 1 on page 10	1 to 7
X	EP0875552 A1 (Procter & Gamble) the Examples	1 to 7
X	EP0601990 A1 (Procter & Gamble) the Examples	1 to 7
X	WO97/06237 A1 (Procter & Gamble) Example 1	1 to 7

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
&	Member of the same patent family		

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